

1352. Polyfluorocycloalkenes. Part V.¹ Fluorination of Alkoxy-polyfluorocycloalkenes by Cobaltic Fluoride

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Cobaltic fluoride fluorination in the vapour phase of a series of alkoxy-polyfluorocycloalkenes (made earlier from addition of alcohols to perfluorocycloalkenes) has given highly fluorinated saturated ethers and negligible amounts of fragmentation products. The ethers so obtained were characterised by fluorine-19 and proton nuclear magnetic resonance spectroscopy. Some of them were cleaved with sulphuric acid to give perfluorocyclohexanone and -pentanone. This provides a useful route to cyclic fluoroketones.

COBALTIC FLUORIDE has found extensive use in the preparation of many saturated polyfluorocarbons.² However, in most cases reported so far, functional groups are not retained in such fluorinations. A few compounds containing oxygen,^{3,4} nitrogen,^{5,6} and sulphur^{7,8} have been fluorinated but the yields of products containing these elements were small. In the present work, advantage has been taken of the apparent stabilising influence of a highly fluorinated substituent on an ether linkage to prepare a series of saturated polyfluoroethers in good yield by cobaltic fluoride fluorination of alkoxy-polyfluorocycloalkenes in the vapour phase.

Alcohols and cyclic fluoro-olefins in the presence of a base gave mixtures of 1- and 3-alkoxy-olefins;⁹ *e.g.*, methanol, potassium hydroxide, and decafluorocyclohexene gave nonafluoro 1- and 3-methoxycyclohexene in the ratio of 7 : 3, respectively.⁹ When the latter isomers were fluorinated, at the same temperature and nitrogen flow-rate, in a small stirred reaction vessel containing cobaltic fluoride, each, as expected, gave an identical mixture containing four components. Thus, in subsequent work, the mono-alkoxy polyfluorocycloalkene mixtures⁹ were fluorinated.

The proportions of the four compounds obtained from the fluorination of the mixed nonafluoro 1- and 3-methoxycyclohexenes were found to depend on temperature and nitrogen flow-rate (the rate of addition of the olefins and the degree of exhaustion of the cobaltic fluoride were kept as constant as possible). The results of fluorinations at different temperatures and nitrogen flow-rates are summarised in Table 1. These results indicate

TABLE I

Cobaltic fluoride fluorination of the mixed nonafluoro 1- and 3-methoxycyclohexenes

Temp.	N ₂ (l./hr.)	(I) (%)	(II) (%)	(III) (%)	(IV) (%)	Starting material (%)
100 ^o	6	0	4.5	44.5	50.0	0
100	5	0	2.0	18.5	80.5	0
100	3.5	0	13.5	42.8	39.6	4.0
120	5	0	24.5	54.5	21.0	0
150	5	1.7	42	35	21.2	0
195	3	12.2	82.5	5.2	0	0
200	3	5.5	56	33	5.5	0

that addition to the double bond is easier than substitution of hydrogen (*cf.* hydrofluorocyclohexenes¹⁰). Thus, by a suitable choice of temperature and nitrogen flow-rate it

¹ Part IV, S. F. Campbell and R. Stephens, preceding Paper.

² M. Stacey and J. C. Tatlow in "Advances in Fluorine Chemistry" (ed. M. Stacey, J. C. Tatlow, and A. G. Sharpe), Butterworths Scientific Publications, London, 1960, p. 176.

³ R. D. Fowler, W. B. Burford, J. M. Hamilton, R. G. Sweet, C. E. Weber, J. S. Kasper, and I. Litant, *Ind. Eng. Chem.*, 1947, **39**, 292.

⁴ F. F. Holub and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1950, **72**, 4879.

⁵ J. Thompson and H. J. Emelús, *J.*, 1949, 3080.

⁶ R. N. Haszeldine, *J.*, 1950, 1638, 1966.

⁷ G. A. Silvey and G. H. Cady, *J. Amer. Chem. Soc.*, 1950, **72**, 3624.

⁸ J. Schultz and M. Hauptschein, *J. Amer. Chem. Soc.*, 1952, **74**, 848.

⁹ A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J.*, 1965, 7358.

¹⁰ R. Stephens, J. C. Tatlow, and E. H. Wiseman, *J.*, 1959, 148.

TABLE 2
 Fluorine-19 n.m.r. spectra

Ether	Band no.	δ	Relative intensity	Assignment
Trifluoromethyl undecafluorocyclohexyl	1	-16.5	3	-CF ₃
	2-7	49.6-72.8	11	Ring fluorines
Difluoromethyl undecafluorocyclohexyl	1	7.2 (doublet; $J_{FH} = 60$ c./sec.)	2	-CF ₂ H
	2	44.4	4	{ AB quadruplet from C-2, C-6
	3	52.4		
	4	57.9		
	5	65.9		
	6	55.7		
	7	64.5	1	C-3, C-4, C-5 C-1
Methyl undecafluorocyclohexyl	1	52.9	4	{ AB quadruplet from C-2, C-6
	2	59.0		
	3	55.1	6	C-3, C-4, C-5
	4	67.8	1	C-1
Fluoromethyl undecafluorocyclohexyl	1-4	41.9-67.8	11	Ring fluorines
	5	75.5 (triplet; $J_{FH} = 50$ c./sec.)	1	-CH ₂ F
1,1,2,2-Tetrafluoroethyl undecafluorocyclohexyl	1	9.4	2	Side chain >CF ₂
	2	52.4	4	{ AB quadruplet from C-2, C-6
	3	58.4		
	4	55.1		
	5	56.2	6	C-3, C-4, C-5
	6	62.3	1	-CF ₂ H
	7	(doublet; $J_{FH} = 66$ c./sec.) 67.3	1	C-1
1,2,2-Trifluoroethyl undecafluorocyclohexyl	1	59.3 (doublet; $J_{FH} = 50$ c./sec.)	2	-CF ₂ H
	2	67.3 (split band)	2	>CHF, C-1
	3-6	44.7-60.1	10	C-2, C-3, C-4, C-5, C-6
1,2-Difluoroethyl undecafluorocyclohexyl	1-4	44.1-58.9	10	C-2, C-3, C-4, C-5, C-6
	5	66.7	2	>CHF, C-1
	6	162.7 (triplet; $J_{FH} = 50$ c./sec.)	1	-CH ₂ F
Pentafluoroethyl undecafluorocyclohexyl	1	9.4	2	Side chain >CF ₂
	2	11.0	3	-CF ₃
	3	52.9	4	{ AB quadruplet from C-2, C-6
	4	57.9		
	5	55.7	6	C-3, C-4, C-5
	6	65.6	1	C-1
1,2,2,2-Tetrafluoroethyl undecafluorocyclohexyl	1	8.8	3	-CF ₃
	2	57.3	10	C-2, C-3, C-4, C-5, C-6
	3	66.7	2	>CHF, C-1
2,2,2-Trifluoroethyl undecafluorocyclohexyl	1	-0.55	3	-CF ₃
	2	52.9	10	C-2, C-3, C-4, C-5, C-6
	3	56.2		
	4	67.8		
1H-Hexafluoro-n-propyl undecafluorocyclohexyl	1	4.8	3	-CF ₃
	2	50.2	2	Side-chain >CF ₂
	3	54.9	1	Side-chain >CHF
	4-9	(doublet; $J_{FH} = 50$ c./sec.) 42.2-55.8	10	C-2, C-3, C-4, C-5, C-6
	10	58.9	1	C-1
1H,3H-Pentafluoro-n-propyl undecafluorocyclohexyl	1	45.4	10	C-2, C-3, C-4, C-5, C-6
	2	47.8		
	3	54.2		

TABLE 2 (Continued)

Ether	Band no.	δ	Relative intensity	Assignment	
1 <i>H</i> ,3 <i>H</i> -Pentafluoro- <i>n</i> -propyl undecafluorocyclohexyl	4	51.8	2	Side chain $>CF_2$	
	5	56.6	2	$-CF_2H$	
	(doublet; $J_{FH} = 50$ c./sec.)				
	6	60.6	3	$>CFH$, C-1	
	2,2,3,3-Tetrafluoro- <i>n</i> -propyl undecafluorocyclohexyl	1	43.0	2	Side chain $>CF_2$
		2	43.0	4	{ AB quadruplet from C-2, C-6
3		46.2			
4		51.0			
5		54.2			
6		47.8	6	C-3, C-4, C-5	
7		55.8	2	$-CF_2H$	
(doublet; $J_{FH} = 50$ c./sec.)					
8	60.0	1	C-1		
Difluoromethyl nonafluorocyclopentyl	1	6.0	2	$-CF_2H$	
	(doublet; $J_{FH} = 70$ c./sec.)				
	2	43.0	4	{ AB quadruplet from C-2, C-5	
	3	46.2			
	4	52.6			
	5	55.8			
	6	48.6	4	{ AB quadruplet from C-3, C-4	
	7	49.1			
8	56.0	1	C-1		
Methyl nonafluorocyclopentyl	1	49.0	4	{ AB quadruplet from C-2, C-5	
	2	58.0			
	3	59.0			
	4	68.0			
	5	60.0	4	C-3, C-4	
	6	68.0	1	C-1	
Fluoromethyl nonafluorocyclopentyl	1	45.0	4	{ AB quadruplet from C-2, C-5	
	2	52.0			
	3	58.0			
	4	65.0			
	5	53.0	4	{ AB quadruplet from C-3, C-4	
	6	54.0			
	7	64.0	1	C-1	
	8	77.0	1	$-CH_2F$	
(triplet; $J_{FH} = 50$ c./sec.)					
Difluoromethyl heptafluorocyclobutyl	1	7.5	2	$-CF_2H$	
	(doublet; $J_{FH} = 50$ c./sec.)				
	2	53.7	4	{ AB quadruplet from C-2, C-4	
	3	56.2			
	4	57.2			
	5	59.7			
	6	58.2	2	C-3	
7	63.8	1	C-1		
Methyl heptafluorocyclobutyl	1	52.7	4	{ AB quadruplet from C-2, C-4	
	2	54.9			
	3	55.5			
	4	58.0			
	5	56.9	2	C-3	
	6	66.0	1	C-1	
Fluoromethyl heptafluorocyclobutyl	1	53.6	4	{ AB quadruplet from C-2, C-4	
	2	55.9			
	3	56.5			
	4	58.8			
	5	57.8	2	C-3	
	6	67.8	1	C-1	
	7	78.9	1	$-CH_2F$	
(triplet; $J_{FH} = 50$ c./sec.)					

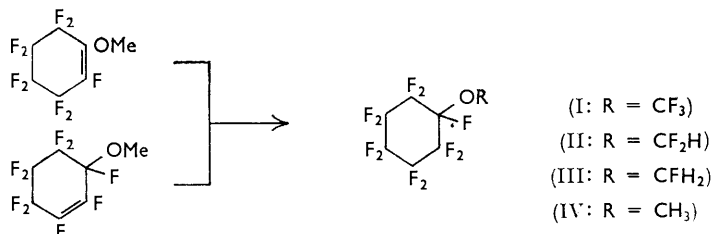
was possible to obtain an optimum yield of a particular compound. As expected, at higher temperatures more fluorine was introduced. The components were readily identified by infrared and n.m.r. spectroscopy. All the components (I)—(IV) were transparent between 2000 and 1500 cm^{-1} , and were therefore saturated, and all except (I) displayed absorption near 3000 cm^{-1} consistent with the presence of hydrogen. The fluorine-19 n.m.r. spectra were particularly valuable in establishing the presence of an undecafluorocyclohexyl ring system in all the components and unequivocally demonstrating the nature of the side chain, as set out in Table 2. The proton n.m.r. spectra provided unambiguous support for the structure of the side chain, as set out in Table 3.

TABLE 3
Proton n.m.r. spectra

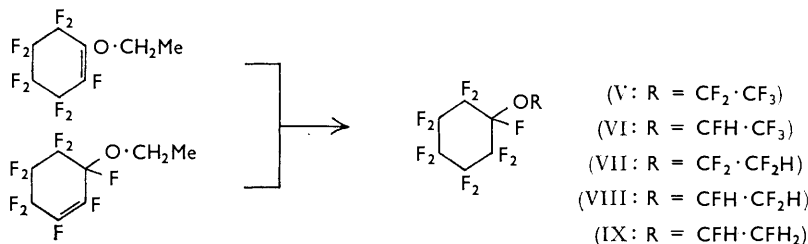
Ether	δ	Splitting	J_{FH} (c./sec.)	Relative intensity	Assignment
Difluoromethyl undecafluorocyclohexyl	6.4	Triplet	75	—	$-\text{CHF}_2$
Methyl undecafluorocyclohexyl	3.6	Broad singlet	—	—	$-\text{CH}_3$
Fluoromethyl undecafluorocyclohexyl	5.3	Doublet	50	—	$-\text{CH}_2\text{F}$
1,1,2,2-Tetrafluoroethyl undecafluorocyclohexyl	5.4	Triplet of triplets	55	—	$-\text{CF}_2\text{CF}_2\text{H}$
1,2,2-Trifluoroethyl undecafluorocyclohexyl	5.55	Doublet	55	1	>CFH
	5.45	Triplet	55	1	$-\text{CF}_2\text{H}$
1,2-Difluoroethyl undecafluorocyclohexyl	5.7	Doublet of quartets	55	1	>CHF
	4.1	Doublet of doublets of doublets	45	2	$-\text{CHFCH}_2\text{F}$
		5		10	
1,2,2,2-Tetrafluoroethyl undecafluorocyclohexyl	5.55	Doublet *	55	—	$-\text{CHFCF}_3$
2,2,2-Trifluoroethyl undecafluorocyclohexyl	3.95	Quadruplet	15	—	$-\text{CH}_2\text{CF}_3$
1 <i>H</i> -Hexafluoro- <i>n</i> -propyl undecafluorocyclohexyl	5.75	Doublet of triplets	53	—	$-\text{CFH}-\text{CF}_2-$
1 <i>H</i> ,3 <i>H</i> -Pentafluoro- <i>n</i> -propyl undecafluorocyclohexyl	5.6	Triplet of triplets	53	1	$-\text{CF}_2\text{CF}_2\text{H}$
	5.75	Doublet of triplets	53	1	$-\text{CHFCF}_2-$
2,2,3,3-Tetrafluoro- <i>n</i> -propyl undecafluorocyclohexyl	4.15	Triplet	12	2	$-\text{CH}_2\text{CF}_2-$
	5.55	Triplet of triplets	53	1	$-\text{CF}_2\text{CF}_2\text{H}$
	4		4		
Difluoromethyl nonafluorocyclopentyl	6.2	Triplet	68	—	$-\text{CF}_2\text{H}$
Methyl nonafluorocyclopentyl	3.5	Broad singlet	—	—	$-\text{CH}_3$
Fluoromethyl nonafluorocyclopentyl	5.15	Doublet	50	—	$-\text{CH}_2\text{F}$
Difluoromethyl heptafluorocyclobutyl	6.0	Triplet of doublets	71	—	$\text{>CF}-\text{OCF}_2\text{H}$
	1.4		1.4		
Heptafluorocyclobutyl methyl	3.4	Doublet	1.8	—	$\text{>CF}-\text{O}-\text{CH}_3$
Fluoromethyl heptafluorocyclobutyl	5.15	Doublet *	50	—	$-\text{CFH}_2$

* With further very weak coupling.

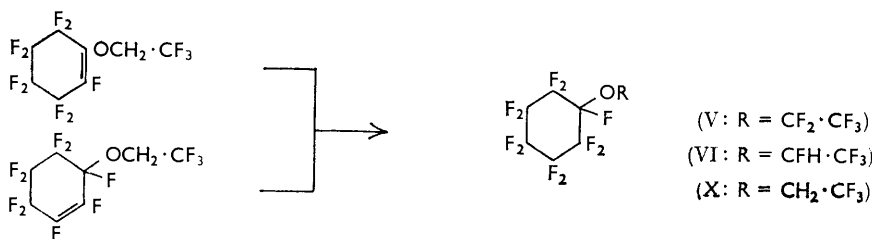
Thus, components (I)—(IV) were shown to be trifluoromethyl-, difluoromethyl-, fluoromethyl-, and methyl undecafluorocyclohexyl ether, respectively. The fluorination of (II) gave (I) in much better yield than could be obtained by fluorination of the mixed olefins; *i.e.*, a recycling procedure gives the best yields of highly fluorinated ethers; above 200° more volatile fragmentation products were formed.



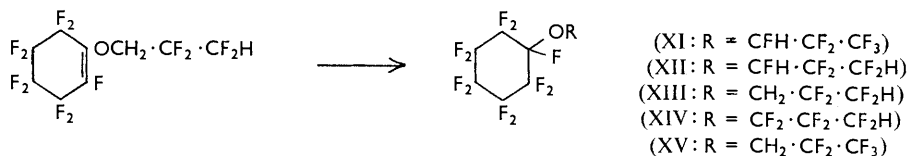
The same type of fluorination of related alkoxy-polyfluoro-olefins⁹ gave a similar range of saturated ethers which were identified by the same techniques (see Tables 2 and 3). Thus, the 1- and 3-ethoxynonafluorocyclohexenes⁹ at 150° gave pentafluoroethyl-, 1,2,2,2-tetrafluoroethyl-, 1,1,2,2-tetrafluoroethyl-, 1,2,2-trifluoroethyl-, and 1,2-difluoroethylundecafluorocyclohexyl ether, (V)—(IX), respectively. This fluorination was the only one in which sufficient of a fragmentation product, *viz.*, dodecafluoro-*n*-pentane, was obtained to permit its identification. The pentafluoro- and 1,2,2,2-tetrafluoro-ethyl ethers, (V) and (VI), were also obtained in the fluorination of the nonafluoro-1- and 3-(2',2',2'-trifluoroethoxy)cyclohexenes.⁹ Fluorination at 100° afforded also 2,2,2-tri-



fluoroethyl undecafluorocyclohexyl ether (X); these ethers were all identified by infrared and n.m.r. spectroscopy as before (Tables 2 and 3).

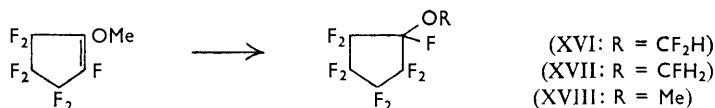


Nonafluoro-1-(2',2',3',3'-tetrafluoro-*n*-propoxy)cyclohexene⁹ was, likewise, fluorinated at 150° to give five products of which three were obtained in a pure state and identified spectroscopically (see Tables 2 and 3) as 1*H*-hexafluoro-*n*-propyl, 1*H*,3*H*-pentafluoro-*n*-propyl, and 2,2,3,3-tetrafluoro-*n*-propyl undecafluorocyclohexyl ether, (XI) (XII), and (XIII), respectively. The other two components could not be separated but were tentatively identified, from the proton n.m.r. spectrum of the mixture, as 3*H*-hexafluoro-*n*-propyl and 1*H*,1*H*-pentafluoro-*n*-propyl undecafluorocyclohexyl ether (XIV) and (XV).

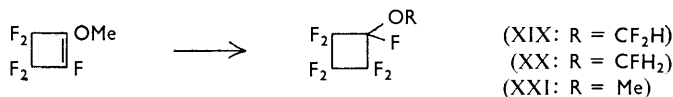


Fluorination of this type of ether, without appreciable fragmentation, was extended to five- and four-membered ring systems. Thus, heptafluoro-1-methoxycyclopentene⁹ was passed over cobaltic fluoride at 90° to give difluoromethyl, fluoromethyl, and methyl nonafluorocyclopentyl ether, (XVI)—(XVIII), respectively.

These structural allocations were based on their fluorine-19- and proton n.m.r. spectra (see Tables 2 and 3).



Similarly, fluorination of pentafluoro-1-methoxycyclobutene⁹ at 150° gave difluoromethyl, fluoromethyl, and methyl heptafluorocyclobutyl ether, (XIX), (XX), and (XXI), respectively; the last has been prepared elsewhere from tetrafluoroethylene and methyl trifluorovinyl ether.¹¹ All the ethers displayed consistent infrared and n.m.r. spectra (see Tables 2 and 3).



An example of the mild fluorination of a purely acyclic ether was provided by 2-chloro-1,1,2-trifluoroethyl methyl ether,¹² which below 100° gave 2-chloro-1,1,2-trifluoroethyl fluoromethyl ether and unchanged starting material without appreciable fragmentation. However, between 100 and 120° several compounds were produced and the carbon recovery was poor; above 120° fragmentation was almost the sole process. From these results it appears that to obtain highly fluorinated ethers from ethers containing more than 50% of hydrogen a recycling process at low temperatures is necessary.

Cleavage of heptafluorocyclobutyl methyl ether by 95% sulphuric acid at 175° has been shown to give hexafluorocyclobutanone.¹¹ In the same way methyl and fluoromethyl undecafluorocyclohexyl ether and methyl nonafluorocyclopentyl ether gave decafluorocyclohexanone and octafluorocyclopentanone, respectively. The latter was previously obtained in poor yield from cyclopentanone and elemental fluorine.⁴ Both ketones were fully characterised by ultraviolet, infrared, and n.m.r. spectroscopy and mass spectrometry.¹³ When treated with semicarbazide, in the usual way, both gave a crystalline adduct which did not undergo elimination to the semicarbazone (cf. hexafluoroacetone¹⁴).

EXPERIMENTAL

Gas Chromatography.—Analytical work was carried out using columns 2 m. long × 4 mm. diam. packed with dinonyl phthalate-kieselguhr (1 : 2) used at 100° and N₂ flow-rate ca. 1.0 l./hr. For preparative-scale work a column 488 cm. × 75 mm., with the same packing as the analytical column, was used.

Infrared Spectra.—These were measured on a Perkin-Elmer Infracord spectrometer over the range 4000—650 cm.⁻¹, and all the ethers obtained were transparent between 2000 and 1500 cm.⁻¹ (saturated systems).

N.m.r. Spectroscopy.—The fluorine-19 spectra were measured on a Mullard SL 44 Mark 1 instrument at 30.107 Mc./sec. The figures quoted are chemical shifts (δ) and are in p.p.m. from trifluoroacetic acid as external reference (see Table 2).

The proton spectra were measured on a Varian instrument at 60 Mc./sec., and the figures quoted are chemical shifts (δ) in p.p.m. from tetramethylsilane as external reference (see Table 3).

Fluorination of the Mixed Nonafluoro-1- and -3-methoxycyclohexenes.—The mixed olefins (34.5 g.; in the ratio, 1- : 3-, 7 : 3) were fluorinated in a stream of nitrogen (5 l./hr.) at 150°, in a small stirred cobaltic fluoride reaction vessel (this nickel vessel was 48 cm. long × 5 cm. diam. and contained ca. 150 g. of cobaltic fluoride) in the usual way.¹⁵ The product was collected at -190° and, after warming to room temperature, was washed successively with aqueous sodium hydrogen carbonate and water, and dried (Na₂SO₄) to give a colourless liquid

¹¹ D. C. England, *J. Amer. Chem. Soc.*, 1961, **83**, 2205.

¹² J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1948, **70**, 1550.

¹³ J. R. Majer, unpublished work.

¹⁴ N. Fukuhara and L. A. Bigelow, *J. Amer. Chem. Soc.*, 1941, **63**, 788.

¹⁵ J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *J.*, 1965, 2382.

(40.6 g.) which was shown by gas chromatography to contain four components; these were separated by preparative scale gas chromatography (65°; N₂ flow-rate 60 l./hr.) to give: (i) *trifluoromethyl undecafluorocyclohexyl ether* (0.5 g.), b. p. 74° (Found: C, 22.9; H, 0.0. C₇F₁₄O requires C, 22.8%); it had no absorption between 3000 and 1650 cm.⁻¹; (ii) *difluoromethyl undecafluorocyclohexyl ether* (12.3 g.), b. p. 84° (Found: C, 24.5; H, 0.0; F, 71.2. C₇HF₁₃O requires C, 24.1; H, 0.3; F, 71.0%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (iii) *methyl undecafluorocyclohexyl ether* (6.2 g.), b. p. 102° (Found: C, 26.9; H, 0.7. C₇H₅F₁₁O requires C, 26.9; H, 1.0%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (iv) *fluoromethyl undecafluorocyclohexyl ether* (10.2 g.), b. p. 103° (Found: C, 25.7; H, 0.6; F, 69.3. C₇H₂F₁₂O requires C, 25.5; H, 0.6; F, 69.1%), ν_{\max} . 3000 and 2900 cm.⁻¹ (\geq CH₂).

Hydrolysis of Methyl Undecafluorocyclohexyl Ether.—The ether (5.6 g.) and sulphuric acid (10 c.c.; 95%) were kept at 190° for 20 hr. in a sealed Pyrex tube, and the contents then distilled to give decafluorocyclohexanone monohydrate (3.2 g.), b. p. 74–75°, ν_{\max} . 3400 and 1620 cm.⁻¹ ("bound" water); distillation from phosphoric oxide gave *decafluorocyclohexanone*, b. p. 56°, ν_{\max} . 1800 cm.⁻¹ (\geq CO), λ_{\max} . (in diethyl ether) 2360 Å (ϵ , 87) (the monohydrate in ether was transparent from 2000 to 4000 Å); the mass spectrum contained a top mass peak at 278 (C₆F₁₀O) and a consistent fragmentation pattern; the ¹⁹F n.m.r. spectrum consisted of two bands at 45 and 58 in the relative intensity of 2 : 3, respectively, arising from the fluorine atoms at C-2 and C-6 and C-3, C-4, and C-5, respectively.

The ketone and semicarbazide gave an *adduct*, m. p. 142–144° (decomp.) (Found: C, 23.9; H, 1.8. C₇H₅F₁₀N₃O₂ requires C, 23.8; H, 1.4%).

Hydrolysis of Fluoromethyl Undecafluorocyclohexyl Ether.—The ether (5.0 g.) and sulphuric acid (10 c.c.; 95%) gave, in the above manner, decafluorocyclohexanone (2.0 g.) with a correct infrared spectrum.

Fluorination of the Mixed 1- and 3-Ethoxynonafluorocyclohexenes (6 : 1, respectively).—The mixed olefins (35.0 g.) were fluorinated in the normal way at 150° (N₂ flow-rate 21 l./hr.) to give a liquid (27.4 g.) which was shown by gas chromatography to contain six components and these were separated (65°; N₂ flow-rate 60 l./hr.) to give: (i) dodecafluoro-n-pentane (2.8 g.) with a correct infrared spectrum; (ii) *pentafluoroethyl undecafluorocyclohexyl ether* (1.4 g.) with a correct infrared spectrum (see later); (iii) *1,2,2-tetrafluoroethyl undecafluorocyclohexyl ether* (2.6 g.) with a correct infrared spectrum (see later); (iv) *1,1,2,2-tetrafluoroethyl undecafluorocyclohexyl ether* (2.8 g.), b. p. 97° (Found: C, 23.9; H, 0.2; F, 71.1. C₈HF₁₅O requires C, 24.1; H, 0.2; F, 71.6%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (v) *1,2,2-trifluoroethyl undecafluorocyclohexyl ether* (6.8 g.), b. p. 112° (Found: C, 25.3; H, 0.5. C₈H₂F₁₄O requires C, 25.3; H, 0.5%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (vi) *1,2-difluoroethyl undecafluorocyclohexyl ether* (1.7 g.), b. p. 122° (Found: C, 26.7; H, 1.1. C₈H₃F₁₃O requires C, 26.5; H, 0.8%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (vii) 1-ethoxy-nonafluorocyclohexene (3.1 g.) with a correct infrared spectrum.

Fluorination of the Mixed Nonafluoro-1- and 3-(2',2',2'-trifluoroethoxy)cyclohexenes (ratio 4 : 1, respectively).—The mixed olefins (25 g.) were fluorinated in a stream of nitrogen (2 l./hr.) in the normal way at 100° to give a liquid (22 g.) which was separated by gas chromatography (70°; N₂ flow-rate 60 l./hr.) to give: (i) *pentafluoroethyl undecafluorocyclohexyl ether* (1.5 g.), b. p. 93° (Found: C, 22.7; H, 0.0; F, 72.6. C₈F₁₆O requires C, 23.1; F, 73.1%); it had no absorption between 3500 and 1500 cm.⁻¹; (ii) *1,2,2,2-tetrafluoroethyl undecafluorocyclohexyl ether* (9.5 g.), b. p. 101° (Found: C, 24.2; H, 0.2. C₈HF₁₅O requires C, 24.1; H, 0.2%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (iii) *2,2,2-trifluoroethyl undecafluorocyclohexyl ether* (5.5 g.), b. p. 106° (Found: C, 25.7; H, 0.6; F, 70.6. C₈H₂F₁₄O requires C, 25.3; H, 0.5; F, 70.0%), ν_{\max} . 3000 cm.⁻¹ (\geq CH).

Fluorination of Nonafluoro-1-(2',2',3',3'-tetrafluoro-n-propoxy)cyclohexene.—This olefin (25 g.) was fluorinated in a stream of nitrogen (3 l./hr.) in the usual way at 150° to give a liquid (24.5 g.) which was separated by gas chromatography (70°; N₂ flow-rate 60 l./hr.) to give: (i) *1H-hexafluoro-n-propyl undecafluorocyclohexyl ether* (2.0 g.), b. p. 120° (Found: C, 24.1; H, 0.3. C₉HF₁₇O requires C, 24.1; H, 0.2%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (ii) a mixture (2.5 g.) containing the suspected *3H-hexafluoro-n-propyl* (50%), *1H-hexafluoro-n-propyl* (25%), and the suspected *1H,1H-pentafluoro-n-propyl* (25%) undecafluorocyclohexyl ethers (assessed by ¹H n.m.r. spectroscopy); (iii) *1H,3H-pentafluoro-n-propyl undecafluorocyclohexyl ether* (12.0 g.), b. p. 133° (Found: C, 25.6; H, 0.6; F, 70.9. C₉H₂F₁₆O requires C, 25.2; H, 0.5; F, 70.7%), ν_{\max} . 3000 cm.⁻¹ (\geq CH); (iv) *2,2,3,3-tetrafluoro-n-propyl undecafluorocyclohexyl ether* (4.0 g.),

b. p. 136° (Found: C, 26.0; H, 0.6. $C_9H_3F_{15}O$ requires C, 26.2; H, 0.7%), ν_{\max} . 3000 cm^{-1} ($\geq CH$).

Fluorination of Heptafluoro-1-methoxycyclopentene.—This olefin (18.0 g.) was fluorinated in a stream of nitrogen (5 l./hr.) in the usual way at 90° to give a liquid product (17.2 g.) which was shown by analytical gas chromatography to contain three components and was separated by preparative scale gas chromatography (65°; N_2 flow-rate 60 l./hr.) to give: (i) *difluoromethyl nonafluorocyclopentyl ether* (0.4 g.), b. p. 71° (Found: C, 24.4; H, 0.4. $C_6HF_{11}O$ requires C, 24.2; H, 0.3%), ν_{\max} . 3000 cm^{-1} ($\geq CH$); (ii) *methyl nonafluorocyclopentyl ether* (6.8 g.), b. p. 81° (Found: C, 27.5; H, 1.2; F, 65.3. $C_6H_3F_9O$ requires C, 27.5; H, 1.2; F, 65.3%), ν_{\max} . 3000 cm^{-1} ($\geq CH$); (iii) *fluoromethyl nonafluorocyclopentyl ether* (6.6 g.), b. p. 78° (Found: C, 25.8; H, 0.7; F, 67.4. $C_6H_2F_{10}O$ requires C, 25.7; H, 0.7; F, 67.8%), ν_{\max} . 3000 cm^{-1} ($\geq CH$).

Hydrolysis of Methyl Nonafluorocyclopentyl Ether.—The ether (5.0 g.) and sulphuric acid (20 c.c.; 95%) were kept together in a sealed Pyrex tube at 175° for 2 hr. The mixture was then treated as for the cyclohexyl analogue to give octafluorocyclopentanone (1.7 g.), b. p. 24° (lit.,⁴ b. p. 24°), ν_{\max} . 1830 cm^{-1} ($\geq CO$); mass spectrometry gave a top mass peak at 228 (C_5F_8O) and a consistent fragmentation pattern. The ^{19}F n.m.r. spectrum consisted of two bands of equal intensity at 51 and 62.

The ketone and semicarbazide gave an adduct, m. p. 184° (decomp.) (lit.,⁴ 185—186°) (Found: C, 23.8; H, 1.6. Calc. for $C_6H_5F_8N_3O_2$: C, 23.8; H, 1.7%).

Fluorination of Pentafluoro-1-methoxycyclobutene.—This compound (36.0 g.) was fluorinated in a stream of nitrogen (4 l./hr.) at 150° in the usual way and the liquid product (35.0 g.) separated by gas chromatography (70°; N_2 flow-rate 60 l./hr.) to give: (i) *difluoromethyl heptafluorocyclobutyl ether* (3.5 g.), b. p. 43—44° (Found: C, 24.4; H, 0.6; F, 69.0. C_5HF_9O requires C, 24.2; H, 0.4; F, 68.9%), ν_{\max} . 2950 cm^{-1} ($\geq CH$); (ii) *heptafluorocyclobutyl methyl ether* (6.5 g.), b. p. 51° (lit.,¹¹ 56°) (Found: C, 28.3; H, 1.5. Calc. for $C_5H_3F_7O$: C, 28.3; H, 1.4%), ν_{\max} . 2950 cm^{-1} ($\geq CH$); (iii) *fluoromethyl heptafluorocyclobutyl ether* (6.0 g.), b. p. 62° (Found: C, 26.1; H, 0.8. $C_5H_2F_8O$ requires C, 26.1; H, 0.9%), ν_{\max} . 2950 cm^{-1} ($\geq CH$); (iv) pentafluoro-1-methoxycyclobutene (11.5 g.) with a correct infrared spectrum.

Fluorination of 2-Chloro-1,1,2-trifluoroethyl Methyl Ether.—This compound¹² (15.0 g.) was fluorinated in a stream of nitrogen (5 l./hr.) at 80° in the usual way to give a liquid (12.3 g.) which was separated by gas chromatography (80°; N_2 flow-rate 60 l./hr.) to give: (i) 2-chloro-1,1,2-trifluoroethyl methyl ether (8.5 g.) with a correct infrared spectrum; (ii) *2-chloro-1,1,2-trifluoroethyl fluoromethyl ether* (1.7 g.), b. p. 79—80° (Found: C, 21.9; H, 1.9; F, 45.0. $C_3H_3ClF_4O$ requires C, 21.6; H, 1.8; F, 45.6%), ν_{\max} . 2950 cm^{-1} ($\geq CH$); the ^{19}F n.m.r. spectrum consisted of an overlapping triplet of triplets ($-CH_2F$) and doublet of triplets ($-CFH-$) of equal total intensities centred at 77.7 and a band at 9.9 ($\geq CF_2$) which was too complex to be analysed. The proton n.m.r. spectrum consisted of a doublet ($J_{HF} = 50$ c./sec.) centred at 5.3 ($-CH_2F$) and a doublet of triplets ($J_{HFgem.} = 50$ c./sec.; $J_{HFvic.} = 5$ c./sec.) centred at 5.9 ($-CF_2-CFHCl$) in the intensity ratio 2 : 1.

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